MECHANISMS OF AMINE TRANSPORT
IN COAL PARTICLES

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INTRODUCTION

There exists considerable evidence in the literature which suggests that the organic phase of coal is a highly crosslinked macromoleular network. This analysis is supported by the fact that the organic phase of coals can swell in thermodynamically compatible solvents to twice its original volume without complete dissolution (Larsen and Kovac, 1978; Lucht and Peppas, 1981 a,b; Lucht, 1983). To aid in the study of the highly crosslinked coal network, Lucht and Peppas (1981a) proposed a simplified description of the organic phase, containing tetrafunctional and multifunctional crosslinks, unreacted functionalities, chain ends, entanglements, chain loops, and effective network chains. Physical crosslinks occur because the system is highly entangled. The chains have limited mobility and therefore are unlikely to disentangle. Chemical crosslinks result from chemical reactions and are stable under a variety of conditions.

Analysis of dynamic swelling results from macromolecular coal networks swollen by good solvents yields important information about solvent-network interactions and the structure of the network. Diffusion studies can be used to determine the thermodynamic state of the network, i.e., whether the network exists in the glassy or rubbery state. It is also possible to determine the type of solvent uptake which occurs in the network. The solvent uptake can occur by Fickian diffusion, anomalous transport, Case-II transport, or Super Case-II transport.

When a macromolecular network such as coal exists in the thermodynamic glassy state all large molecular chain motions are restricted, but the segmental motions are not necessarily limited. As the temperature of the network is increased to the glass transition temperature, large molecular chain motions become inportant and the network shifts to its thermodynamic rubbery state. The exact glass transition temperature of the macromolecular network is dependent on its chemical and physical nature. The presence of solvent can increase large molecular chain motions at lower temperatures thereby effectively lowering the glass transition temperature of the network. Anomalous diffusion occurs only below the glass transition temperature and at fairly high penetrant activities. Fickian diffusion occurs both in the glassy state and the rubbery state. Concentration-independent Fickian diffusion occurs generally at low penetrant activities or low temperatures.

A convenient method used in the analysis of sorption data employs fitting the sorption data to equation (1).

$$\frac{M_t}{M_\infty} = kt^n \tag{1}$$

Here M_t is defined as the mass of solvent uptake at time t, M_∞ is the mass of solvent uptake as time approaches infinity, k is a constant dependent on the structural characteristics of the network, and n is the exponent which indicates the type of solvent uptake. Table 1 relates the exponent n to the various types of diffusion.

Table 1.

Table 1.
Analysis of diffusional behavior using equation (1)

Exponent n	Type of diffusion
0.5	Fickian diffusion
$0.5 < n < 1.0$	Anomalous transport
1.0	Case-II transport
> 1.0	Super Case-II transport

Equation (1) is valid only in the analysis of the first 60% of the final mass of solvent uptake. It also cannot be used to analyze inflections or overshoots.

For Fickian diffusion with constant boundary conditions and a constant diffusion coefficient, the sorption and desorption kinetics in spheres is given by equation (2) (Crank, 1975).

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\,\exp(-Dn^2\pi^2t/r^2) \tag{2}$$

Here M_t is the mass of solvent uptake at time t, M_∞ is the mass of solvent uptake as time approaches infinity, r is the radius of the sphere, and D is the concentration-independent diffusion coefficient. An important approximate solution to equation (2) at $M_t/M_\infty = 0.5$ is given by equation (3).

$$D = \frac{0.00766d^2}{t_{1/2}} \tag{3}$$

Here $t_{1/2}$ is the diffusional half-time in seconds and d is the sphere diameter in centimeters. Equation (3) gives a useful relationship for the calculation of the diffusion coefficient in cm^2/sec.

For Case-II transport which usually occurs at high penetrant activity and is relaxation-controlled, the desorption and sorption data in a sphere are expressed by equation (4) (Enscore et $al.$, 1977).

$$\frac{M_t}{M_\infty} = 1 - \left(1 - \frac{k_o t}{C_o r}\right)^3 \tag{4}$$

Here k_o is defined as the Case-II relaxation constant in mg/cm^2 min and is assumed to be a constant; C_o is the equilibrium concentration of the penetrant and r is the radius of the sphere.

Most diffusion data do not follow Fickian diffusion or Case-II transport kinetics but are explained by a combination of the two kinetic models. Anomalous transport may be described by coupling of the relaxation process with the diffusion process. This idea of coupling led Berens and Hopfenberg (1978) to propose a model to describe this process; the model is given in equation (5).

$$1 - \frac{M_t}{M_\infty} = \phi_F\left[\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\,\exp(-4\pi^2n^2Dt/d^2)\right] + \phi_R\,\exp(-kt) \tag{5}$$

Here ϕ_F and ϕ_R are the fractions of sorption contributed by Fickian diffusion and the relaxation process respectively, D is the diffusion coefficient for the Fickian portion of the transport, and k is the first-order relaxation constant. If diffusion occurs rapidly in comparison to the relaxation, both D and k can be determined from the sorption data (Enscore et $al.$, 1977).

EXPERIMENTAL PART

The coal samples, packed under nitrogen, were supplied by the Pennsylvania State University Coal Bank. The samples were sieved to the desired mesh size and stored in nitrogen until use.

Untreated coal samples of 1-2 g were dried and weighed to ± 0.005 g on a Mettler top loading balance. The samples were then placed in 10 ml beakers which were suspended in a dessicator over a pool of solvent. The solvents used in the studies were n-propylamine, butylamine, diethylamine, and dipropylamine. The dessicator was sealed and suspended in a water bath to maintain a constant temperature of 35 ± 0.5°C. At set time intervals, the coal samples were removed, weighed, and then returned to the dessicator.

RESULTS AND DISCUSSION

Dynamic swelling studies were performed on seven untreated coal samples. In the first set of experiments, the effect of carbon content on the sorption of n-propylamine vapor was studied. The samples were prepared for experimentation by drying, and then exposed to n-propylamine vapor at 35°C until equilibrium swelling had been reached. The mass of solvent uptake per mass of coal sample (dmmf) was calculated as a function of time. The results for PSOC 418 with 69.94%C (dmmf), PSOC 312 with 78.38%C (dmmf), and PSOC 9129 with 88.19%C (dmmf) are shown in Figure 1. The results for PSOC 791 with 72.25%C (dmmf), PSOC 853 with 80.12%C (dmmf), and PSOC 402 with 82.48%C (dmmf) are shown in Figure 2.

The first major observation from this set of experiments was the dramatic effect of carbon content on the final solvent uptake per mass of coal sample (dmmf). This is shown graphically in Figure 3. The solvent uptake is shown to decrease with increasing carbon content.

The mathematical analysis of the sorption data initially involved fitting the data to equation (3) for the first 60% of the final solvent mass uptake. The results from this analysis are tabulated in Table 2. The results show no direct correlation between carbon content and exponent n; however, all the values fall between 0.5 and 1.0 and therefore all the sorption processes may be classified as anomalous transport.

Table 2.

Analysis of the Sorption Data from Dynamic
Swelling Studies for n-Propylamine using Equation (1)

PSOC	%C (dmmf)	k	Exponent n	r
418	69.94	.07	.74	.998
791	72.25	.05	.83	.999
247	75.53	.024	.981	.993
312	78.38	.05	.79	.993
853	80.23	.04	.79	.996
402	82.48	.05	.68	.994

The model of Berens and Hopfenberg given in equation (1.10) was used to determine diffusion coefficients and relaxation constants. The results from this analysis are tabulated in Table 3. Here both the relaxation constants and the diffusion coefficients are found to decrease with increasing carbon content.

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Table 3.

Diffusion Coefficients and Relaxation Constants
from the n-Propylamine Studies

PSOC	%C (dmmf)	k (sec^{-1})	D(cm^2/sec)
418	69.94	1.1×10^{-6}	7.5×10^{-9}
791	72.25	5.5×10^{-6}	2.8×10^{-9}
247	75.53	6.2×10^{-6}	2.2×10^{-9}
312	78.38	7.9×10^{-6}	3.2×10^{-9}
853	80.12	5.8×10^{-6}	2.2×10^{-9}
402	82.48	4.3×10^{-6}	5.6×10^{-9}

The final mathematical analysis of this data involved calculating the Case-II relaxation constant using the relaxation controlled model given by equation (4). The results from this analysis are tabulated in Table 4. Here the calculated relaxation constants show a decrease as the carbon content increass.

Table 4.

Case-II Relaxation Constants for
n-Propylamine Studies Using Equation (4)

PSOC	%C (dmmf)	k$_o$(g/cm^{2}sec)
418	69.94	5.1×10^{-7}
791	72.25	3.0×10^{-7}
247	75.53	3.1×10^{-7}
312	78.38	2.7×10^{-7}
853	80.12	2.8×10^{-7}
402	82.48	1.6×10^{-7}

The second set of experiments were designed to determine the effect of particle size on solvent transport. Again the samples were pre-dried and then exposed to n-propylamine vapor at 35°C until equilibrium swelling had been reached. The results from these experiments were plotted as the mass of solvent uptake per mass of coal sample (dmmf) as a function of time; these results are given in Figure 4, for PSOC 312 with 78.38%C (dmmf) with sizes of 850-600 μm, 600-425 μm, 425-250 μm, 250-180 μm, and 180-150 μm.

The results from the analysis of exponent n using equation (1) are tabulated in Table 5. A decrease in particle size has a resulting decrease in the value of the exponent n; there is a shift from anomalous transport in the larger particles to Fickian diffusion in the smaller particles.

Table 5

Analysis of the Sorption Data for Varying Particles (PSOC 312)
Sizes Using Equation (1)

Particle Size	k	Exponent n	r
850-600 μm	.05	.79	.993
600-425 μm	.07	.72	.997
425-250 μm	.10	.67	.997
250-180 μm	.12	.62	.999
180-150 μm	.13	.54	.998

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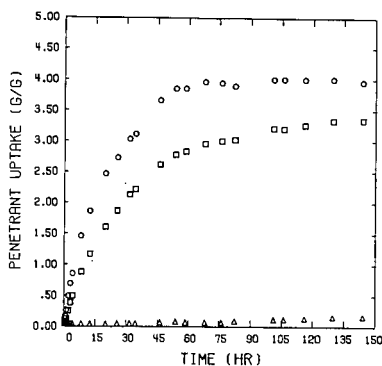
Figure 1: Uptake of n-Propylamine Vapor at 35°C a Function of Time for PSOC 418 (69.94%C $\bigcirc$), PSOC 312 (78.38%C, $\square$) and PSOC 989 (88.19%C, $\triangle$).
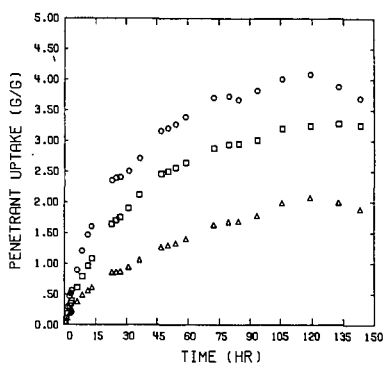
Figure 2: Uptake of n-Propylamine Vapor at 35° as a Function of Time for PSOC 791 (72.25%C, ◯), PSOC 853 (10.12%C, □) and PSOC 402 (81.48%C, △).
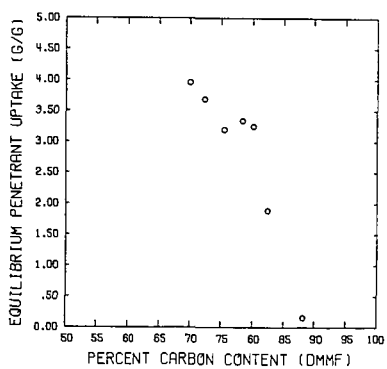

Figure 3: Final Solvent Uptake as a Function of Carbon Content for n-Propylamine Studies.
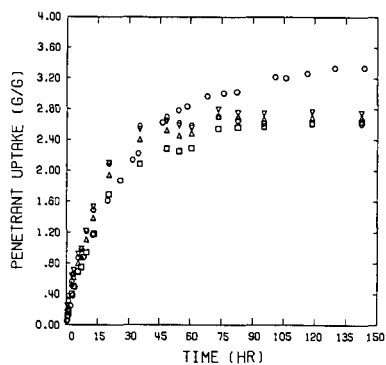
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Figure 4: Uptake of n-Propylamine Vapors by Coal Particles as a Function of Time. Studies with PSOC 312 (78.38%C) and with Particles Sizes of 850-600 μm(○), 600-425 μm (□), 425-250 μm (△), 250-180 μm (◖), and 180-150 μm (▽).

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